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(54) **NOx sensor and method of measurement of NOx concentration**

NOx-Sensor und Verfahren zur NOx-Konzentrationsmessung

Capteur pour NOx et méthode de mesure de la concentration de NOx

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**Description**Background of the Invention

## (1) Field of the Invention

**[0001]** The present invention relates to an NOx sensor having a sensor element made of an oxide, a resistance of which is varied in response to an NOx component in a gas to be measured, and measuring means for measuring resistance of the sensor element for detecting NOx concentration in the gas to be measured.

## (2) Related Art Statement

**[0002]** As a method of measuring an NOx concentration in a gas to be measured such as exhaust gas from an incineration, which includes an NOx component such as nitrogen oxide, there is known a method of sampling a gas to be measured including an NOx component in for example a dust chimney, and measuring an NOx concentration of the sampled gas by means of an optical measuring apparatus. However, the optical measuring apparatus is expensive, and its responsiveness is poor since the sampling operation is necessary.

**[0003]** In order to eliminate the drawbacks mentioned above, a direct insertion type semiconductor sensor is used recently. For example, in Japanese Patent Laid-Open Publication No. 6-222028, an NOx sensor comprising a response portion made of an oxide having a predetermined perovskite structure, and a conductivity measuring portion for measuring a conductivity of the response portion is disclosed.

**[0004]** However, also in the direct insertion type semiconductor sensor mentioned above, there is no countermeasure for an influence of O<sub>2</sub> and CO components included in the gas to be measured with respect to the measured NOx concentration. Moreover, in the response portion, resistance varies in response to an amount of NOx (NO<sub>2</sub>+NO) i.e. a concentration thereof. However, if the ratio of amount (concentration) between NO<sub>2</sub> and NO i.e. the ratio of partial pressure between NO<sub>2</sub> and NO is varied, the resistance measured by the response portion is varied even for the same NOx amount. In this case, it is not the case that only the NOx component is selectively measured. Therefore, in the direct insertion type semiconductor sensor mentioned above, there is a drawback that the NOx concentration in the gas to be measured cannot be selectively measured in a highly precise manner, while the semiconductor sensor is cheap and shows excellent responsiveness as compared with the optical measuring apparatus.

**[0005]** US-A-4840913 describes a NOx detector in which the gas being detected contacts a heated catalyst which oxidizes NO to NO<sub>2</sub> and oxidizes reducing gases such as CO, H<sub>2</sub>, hydrocarbons and alcohols, before contacting a non-selective oxide of nitrogen sensor which is made of SnO<sub>2</sub> or ZnO. Change of resistance of the sensor is sensed.

Summary of the Invention

**[0006]** An object of the present invention is to eliminate the drawbacks mentioned above and to provide an NOx sensor which can measure an NOx concentration in a gas to be measured selectively in a precise manner.

**[0007]** According to the invention, there is provided a NOx sensor as set out in claim 1.

**[0008]** In this construction, since the gas to be measured passes the catalyst which brings the partial pressure ratio of NO/NO<sub>2</sub> to an equilibrium state, and is then contacted with the sensor element under the condition that temperatures of the sensor element and the catalyst are maintained in a constant state by means of the heater, it is possible to perform a high precision measurement. Further, the relation between resistance measured by the sensor element and NOx concentration is determined in response to an O<sub>2</sub> concentration. Therefore, if the O<sub>2</sub> concentration is measured by the O<sub>2</sub> sensor for an adjustment and the NOx concentration is determined from the resistance value in response to the thus measured O<sub>2</sub> concentration, it is possible to perform a high precision measurement. Moreover, since the catalyst has a function for removing a CO component from the gas to be measured, it is possible to measure the NOx concentration with no CO influence.

**[0009]** According to the invention, there is also provided a method of measurement of NO<sub>x</sub> concentration as set out in claim 7.

Brief Description of the Drawing**[0010]**

Fig. 1 is a schematic view for explaining one concept of an NOx sensor according to the invention; and Fig. 2 is a graph showing a relation between a resistance value measured in the NOx sensor and an NOx concentration according to the invention.

Description of the Preferred Embodiments

[0011] Fig. 1 is a schematic view for explaining one concept of an NOx sensor according to the invention. In Fig. 1, an NOx sensor according to the invention comprises a response portion 1 and a measuring portion 2. The response portion 1 is set in a dust chimney 3 through which a gas to be measured flows. The response portion 1 is constructed by arranging, from an upstream side of a flow of the gas to be measured, a catalyst 6, a heater for a temperature adjustment 7, a sensor element 8 and an O<sub>2</sub> sensor 9, all of which are arranged in an alumina protection tube 5 having a gas inlet portion 4. The measuring portion 2 is constructed by arranging a digital multimeter 10 for the sensor element 8, a digital multimeter 11 for the O<sub>2</sub> sensor 9 and a processing portion 12. Moreover, a numeral 13 is a constant-potential power supply of the heater for a temperature adjustment.

[0012] The catalyst 6 is used for making a partial pressure ratio of NO/NO<sub>2</sub> to an equilibrium state and for removing a CO component from the gas to be measured. In this embodiment, the catalyst 6 is integrally formed, but it is possible to form the catalyst 6 separately corresponding to the objects mentioned above respectively. In the case of constructing the catalyst 6 separately, not only the same kinds of catalysts but also the other kinds of catalysts may be used for the catalyst 6. In order to achieve the objects mentioned above, it is preferred to use precious metals or oxides as the catalyst 6. As the precious metals, it is preferred to use platinum, rhodium or gold. As the oxides, it is preferred to use manganese oxide, cobalt oxide or tin oxide.

[0013] The heater for a temperature adjustment 7 is used for maintaining the sensor element 8 and the catalyst 6 always at a constant temperature even if a temperature of the gas to be measured is varied. Therefore, it is preferred to arrange the heater for a temperature adjustment 7 between the sensor element 8 and the catalyst 6. The sensor element 8 is made of an oxide, a resistance of which is varied in response to an NOx component, if the oxide is contacted to the gas to be measured including an NOx component. As the oxide mentioned above, it is preferred to use metal oxide semiconductors. Among them, it is further preferred to use SnO<sub>2</sub>, TiO<sub>2</sub> or In<sub>2</sub>O<sub>3</sub>. If the sensor element 8 is made of the oxides mentioned above, it is possible to use the same structure, shape and so on as those of the known sensor element.

[0014] In the NOx sensor according to the invention having the construction mentioned above, an NOx concentration measuring is performed as follows. At first, the gas to be measured is supplied from the gas inlet portion 4 into the response portion 1 under such a condition that temperatures of the sensor element 8 and the catalyst 6 are maintained constantly by means of the heater for a temperature adjustment 7. The thus supplied gas is passed through the catalyst 6. If the gas to be measured is passed through the catalyst 6, a partial pressure ratio of NO/NO<sub>2</sub> in the gas to be measured becomes an equilibrium state and a CO component in the gas to be measured is burnt. Therefore, the gas to be measured, in which the partial pressure ratio of NO/NO<sub>2</sub> is an equilibrium state and a CO component is removed, can be contacted with the sensor element 8.

[0015] In this case, a relation between a resistance of the sensor element 8 and NOx concentration can be determined one by one if an oxygen concentration is constant. However, the oxygen concentration in the gas to be measured is not constant actually. Therefore, in the present invention, the O<sub>2</sub> sensor 9 is arranged in the response portion 1 so as to always measure the oxygen concentration, and the NOx concentration is obtained from a relation between the resistance of the sensor element 8 based on the oxygen concentration and the NOx concentration. As one example, a relation between resistances at the oxygen concentrations of 1% and 20% and NOx concentrations, which is based on the results in the following experiment 1 of sample Nos. 1-10, is shown by Fig. 2. In Fig. 2, the relation is shown only at the oxygen concentrations 1% and 20%. However, if relations at the other oxygen concentrations are measured beforehand, the NOx concentration can be measured by using the relation corresponding to the oxygen concentration measured by the O<sub>2</sub> sensor 9. As a result, the NOx concentration can be measured without being affected by the partial pressure ratio of NO/NO<sub>2</sub>, the O<sub>2</sub> component, the CO component and the atmospheric temperature.

[0016] Hereinafter, an actual embodiment will be explained.

Experiment 1

[0017] As shown in Fig. 1, the NOx sensor was constructed by arranging the catalyst 6, the heater for a temperature adjustment 7, the sensor element 8 and the O<sub>2</sub> sensor 9. The sensor element 8 was produced according to the following steps. At first, tin chloride was subjected to a hydrolysis by using an ammonia solution to obtain a dissolved solution. Then, the dissolved solution was separated by a filtering. After that, the thus separated dissolved solution was subjected to a pyrolysis at 600°C for 2 hours to synthesize tin oxide powders. Then, the thus obtained tin oxide powders were mixed in a wet state in ethanol solution for 10 hours by using zirconia balls to obtain an tin oxide slurry for dipping. As a body of the sensor element 8, use was made of an alumina tube having a diameter of 1.5 mm and a length of 5 mm to which a platinum wire having a diameter of 3 mm was secured. Then, the body was dipped in the tin oxide slurry. After that, the thus dipped body was fired at 800°C for 2 hours to obtain the sensor element 8.

[0018] Moreover, the heater for a temperature adjustment 7 was produced by working a platinum wire into a coil

shape. Further, platinum powders were arranged on a cordierite honeycomb carrier by a washcoat method. After that, the cordierite honeycomb carrier was fired at 500°C for 2 hours to obtain the catalyst 6 which functions to control the partial pressure ratio of NO/NO<sub>2</sub> and remove the CO component. As the O<sub>2</sub> sensor 9, use was made of a zirconia O<sub>2</sub> sensor. The measurement was performed in such a manner that a resistance of the sensor element 8 and a current of the O<sub>2</sub> sensor 9 were detected respectively by the digital multimeters 10 and 11 via the platinum lead wires.

[0019] As shown in the following Table 1, the gas to be measured including NOx such as NO<sub>2</sub> and NO having a predetermined concentration as well as the other components such as O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, CO and N<sub>2</sub> was prepared. In this case, a total of all components was 100%. Then, the thus prepared gas was flowed, under such a condition that a temperature of the sensor element 8 was maintained constantly, to measure a resistance of the sensor element 8 by using the NOx sensor having the construction mentioned above. Moreover, as a comparative example, a resistance of the sensor element 8 was measured in the same manner as the example mentioned above except that a temperature of the sensor element 8 is not controlled and the catalyst 6 is not used. The results were shown in Table 1.

Table 1

Sample No.	Sensor temperature (°C)	Atmosphere temperature (°C)	NO/NO <sub>2</sub> catalyst	CO burning catalyst	NO <sub>2</sub> (ppm)	NO (ppm)	NOx (ppm)	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	H <sub>2</sub> O (%)	CO (ppm)	N <sub>2</sub>	Resistance (kΩ)
Example of Present Invention	1	500	400	Pt	200	800	1000	1	10	7	0	remainder	76.1
	2	500	400	Pt	100	400	500	1	10	7	0	remainder	72.0
	3	500	400	Pt	50	200	250	1	10	7	0	remainder	66.5
	4	500	400	Pt	10	40	50	1	10	7	0	remainder	41.2
	5	500	400	Pt	2	8	10	1	10	7	0	remainder	10.0
	6	500	400	Pt	200	800	1000	20	10	7	0	remainder	169.1
	7	500	400	Pt	100	400	500	20	10	7	0	remainder	161.0
	8	500	400	Pt	50	200	250	20	10	7	0	remainder	153.2
	9	500	400	Pt	10	40	50	20	10	7	0	remainder	112.3
	10	500	400	Pt	2	8	10	20	10	7	0	remainder	38.0
	11	500	400	Pt	100	400	500	1	10	7	1000	remainder	71.8
	12	500	400	Pt	50	200	250	1	10	7	1000	remainder	66.3
	13	500	400	Pt	200	800	1000	20	10	7	1000	remainder	168.8
	14	500	400	Pt	100	400	500	1	10	7	0	remainder	72.1
	15	500	400	Pt	100	400	500	1	10	20	0	remainder	72.0
	16	500	400	Pt	40	10	50	1	10	7	0	remainder	41.0
	17	500	400	Pt	800	200	1000	1	10	7	0	remainder	76.0
	18	500	400	Pt	800	200	1000	20	10	7	0	remainder	170.0
	19	500	300	Pt	200	800	1000	1	10	7	0	remainder	76.0
	20	500	300	Pt	200	800	1000	20	10	7	0	remainder	169.7
	21	500	300	Pt	800	200	1000	1	10	7	0	remainder	76.2
Comparative Example	1	not control	400	None	200	800	1000	1	10	7	0	remainder	462.3
	2	not control	400	None	200	800	1000	1	10	7	1000	remainder	91.2
	3	not control	400	None	200	800	1000	20	10	7	0	remainder	997.5
	4	not control	400	None	800	200	1000	1	10	7	0	remainder	534.8
	5	not control	300	None	200	800	1000	1	10	7	0	remainder	1676

[0020] From the results shown in Table 1, when the oxygen concentration is constant, it is understood that the same resistance can be always obtained in the examples according to the invention even if a concentration ratio between  $\text{NO}_2$  and NO is varied and also the CO component is included. On the other hand, it is understood that the resistances are largely varied in the comparative examples. Therefore, in the examples according to the invention, if the NOx concentration is measured from the resistance, the constant NOx concentration can be always obtained even if a concentration ratio between  $\text{NO}_2$  and NO is varied and also the CO component is included. Accordingly, the precise measurement can be performed. On the other hand, in the comparative examples, even if the NOx concentration is measured from the resistance, the constant NOx concentration cannot be obtained, and thus the measurement accuracy becomes lower.

#### Experiment 2

[0021] The NOx concentration measuring was performed in the same manner as that of the experiment 1 by using the substantially same NOx sensor as that of the experiment 1 except that an indium oxide obtained by subjecting a nitrate to a pyrolysis at  $600^\circ\text{C}$  for 2 hours was used as a material of the sensor element 8, a manganese oxide was used as the catalyst 6 for controlling the partial pressure ratio of NO/ $\text{NO}_2$ , and a tin oxide was used as the catalyst 6 for removing the CO component. The results were shown in Table 2.

Table 2

Sample No.	Sensor temperature (°C)	Atmosphere temperature (°C)	NO/NO <sub>2</sub> catalyst	CO burning catalyst	NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>x</sub> (ppm)	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	H <sub>2</sub> O (%)	CO (ppm)	N <sub>2</sub>	Resistance (kΩ)
1	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	200	800	1000	1	10	7	0	remainder	3.54
2	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	100	400	500	1	10	7	0	remainder	3.11
3	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	50	200	250	1	10	7	0	remainder	2.23
4	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	10	40	50	1	10	7	0	remainder	1.10
5	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	2	8	10	1	10	7	0	remainder	0.21
6	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	200	800	1000	20	10	7	0	remainder	9.02
7	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	100	400	500	20	10	7	0	remainder	8.34
8	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	50	200	250	20	10	7	0	remainder	7.22
9	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	10	40	50	20	10	7	0	remainder	3.12
10	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	2	8	10	20	10	7	0	remainder	0.63
11	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	100	400	500	1	10	7	1000	remainder	3.13
12	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	50	200	250	1	10	7	1000	remainder	2.24
13	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	200	800	1000	20	10	7	1000	remainder	9.04
14	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	100	400	500	1	10	7	0	remainder	3.11
15	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	100	400	500	1	10	20	0	remainder	3.12
16	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	40	10	50	1	10	7	0	remainder	1.12
17	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	800	200	1000	1	10	7	0	remainder	3.56
18	500	400	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	800	200	1000	20	10	7	0	remainder	9.00
19	500	300	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	200	800	1000	1	10	7	0	remainder	3.55
20	500	300	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	200	800	1000	20	10	7	0	remainder	9.01
21	500	300	Mn <sub>3</sub> O <sub>4</sub>	SnO <sub>2</sub>	800	200	1000	1	10	7	0	remainder	3.56
1	not control	400	None	None	200	800	1000	1	10	7	0	remainder	18.54
2	not control	400	None	None	200	800	1000	1	10	7	1000	remainder	5.50
3	not control	400	None	None	200	800	1000	20	10	7	0	remainder	46.98
4	not control	400	None	None	800	200	1000	1	10	7	0	remainder	24.38
5	not control	300	None	None	200	800	1000	1	10	7	0	remainder	35.46

[0022] Also from the results shown in Table 2, when the oxygen concentration is constant, it is understood that the same resistance can be always obtained in the examples according to the invention even if a concentration ratio between  $\text{NO}_2$  and NO is varied and also the CO component is included. On the other hand, it is understood that the resistances are largely varied in the comparative examples.

Experiment 3

[0023] The NOx concentration measuring was performed in the same manner as that of the experiment 1 by using the substantially same NOx sensor as that of the experiment 1 except that a titanium oxide obtained by subjecting a sulfate to a pyrolysis at 800°C for 1 hour was used as a material of the sensor element 8, a cobalt oxide was used as the catalyst 6 for controlling the partial pressure ratio of NO/NO<sub>2</sub>, and a gold was used as the catalyst 6 for removing the CO component. The results were shown in Table 3.



Table 3

Sample No.	Sensor temperature (°C)	Atmosphere temperature (°C)	NO/NO <sub>2</sub> catalyst	CO burning catalyst	NO <sub>2</sub> (ppm)	NO (ppm)	NOx (ppm)	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	H <sub>2</sub> O (%)	CO (ppm)	N <sub>2</sub>	Resistance (kΩ)
1	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	200	800	1000	1	10	7	0	remainder	23611
2	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	100	400	500	1	10	7	0	remainder	19872
3	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	50	200	250	1	10	7	0	remainder	15181
4	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	10	40	50	1	10	7	0	remainder	6429
5	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	2	8	10	1	10	7	0	remainder	760
6	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	200	800	1000	20	10	7	0	remainder	56262
7	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	100	400	500	20	10	7	0	remainder	47351
8	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	50	200	250	20	10	7	0	remainder	36201
9	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	10	40	50	20	10	7	0	remainder	15210
10	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	2	8	10	20	10	7	0	remainder	1811
11	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	100	400	500	1	10	7	1000	remainder	19869
12	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	50	200	250	1	10	7	1000	remainder	15182
13	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	200	800	1000	20	10	7	1000	remainder	56259
14	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	100	400	500	1	10	7	0	remainder	19870
15	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	100	400	500	1	10	20	0	remainder	19874
16	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	40	10	50	1	10	7	0	remainder	6430
17	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	800	200	1000	1	10	7	0	remainder	23613
18	500	400	Co <sub>3</sub> O <sub>4</sub>	Au	800	200	1000	20	10	7	0	remainder	56259
19	500	300	Co <sub>3</sub> O <sub>4</sub>	Au	200	800	1000	1	10	7	0	remainder	23610
20	500	300	Co <sub>3</sub> O <sub>4</sub>	Au	200	800	1000	20	10	7	0	remainder	56263
21	500	300	Co <sub>3</sub> O <sub>4</sub>	Au	800	200	1000	1	10	7	0	remainder	23616
1 not control	400	400	None	None	200	800	1000	1	10	7	0	remainder	35125
2 not control	400	400	None	None	200	800	1000	1	10	7	1000	remainder	3864
3 not control	400	400	None	None	200	800	1000	20	10	7	0	remainder	87540
4 not control	400	400	None	None	800	200	1000	1	10	7	0	remainder	98734
5 not control	300	300	None	None	200	800	1000	1	10	7	0	remainder	78654

[0024] Also from the results shown in Table 3, when the oxygen concentration is constant, it is understood that the same resistance can be always obtained in the examples according to the invention even if a concentration ratio between NO<sub>2</sub> and NO is varied and also the CO component is included. On the other hand, it is understood that the resistances are largely varied in the comparative example.

[0025] As clearly understood from the above, according to the invention, since the gas to be measured passed through the catalyst which makes a partial pressure ratio of NO/NO<sub>2</sub> to an equilibrium state is contacted to the sensor element under such a condition that temperatures of the sensor element and the catalyst are maintained in a constant state by means of the heater, it is possible to perform a high precision measurement. That is to say, under such a condition mentioned above, a relation between a resistance measured by the sensor element and an NO<sub>x</sub> concentration is determined one by one in response to an O<sub>2</sub> concentration. Therefore, if the O<sub>2</sub> concentration is measured by the O<sub>2</sub> sensor for an adjustment and the NO<sub>x</sub> concentration is determined from the resistance value in response to the thus measured O<sub>2</sub> concentration, it is possible to perform a high precision measurement. Moreover, since the catalyst has a function for removing a CO component from the gas to be measured, a CO component can be removed from the gas to be measured if the gas is contacted with the sensor element, and thus it is possible to measure the NO<sub>x</sub> concentration with no CO influence.

### Claims

#### 1. A NO<sub>x</sub> sensor having

a sensor element (8) made of an oxide, the resistance of which varies in dependence on the NO<sub>x</sub> concentration of a gas to be measured,  
 measuring means (2) for measuring the resistance of the sensor element (8) and thereby detecting the NO<sub>x</sub> concentration of the gas to be measured,  
 a catalyst (6) arranged upstream with respect to said sensor element in a flow direction of the gas to be measured, said catalyst being adapted, when contacted by the gas to be measured, to bring the partial pressure ratio of NO and NO<sub>2</sub> in the gas to equilibrium and to remove CO from the gas,  
 a heater (7) arranged in relation to the sensor element (8) and catalyst (6) for maintaining constant temperature of the sensor element and the catalyst, and  
 an O<sub>2</sub> sensor (9) for detecting the O<sub>2</sub> concentration of the gas to be measured,  
 wherein said measuring means (2) is arranged to perform an adjustment of the measurement value from the sensor element (8) on the basis of the O<sub>2</sub> concentration detected by said O<sub>2</sub> sensor, to determine the NO<sub>2</sub> concentration of the gas.

2. A NO<sub>x</sub> sensor according to claim 1, wherein said oxide of the sensor element (8) is a metal oxide semiconductor.

3. A NO<sub>x</sub> sensor according to claim 2, wherein said metal oxide semiconductor is SnO<sub>2</sub>, TiO<sub>2</sub> or In<sub>2</sub>O<sub>3</sub>.

4. A NO<sub>x</sub> sensor according to claim 1, 2 or 3 wherein said catalyst (6) is a precious metal or an oxide.

5. A NO<sub>x</sub> sensor according to claim 4, wherein said catalyst (6) is a precious metal selected from platinum, rhodium and gold.

6. A NO<sub>x</sub> sensor according to claim 5, wherein said catalyst (6) is a manganese oxide, a cobalt oxide or a tin oxide.

7. A method of measurement of NO<sub>x</sub> concentration, using a sensor according to any one of the preceding claims.

### Patentansprüche

#### 1. NO<sub>x</sub>-Sensor, der aufweist:

ein Sensorelement (8) aus einem Oxid, dessen Widerstand in Abhängigkeit von der NO<sub>x</sub>-Konzentration eines zu messenden Gases variiert,

Messmittel (2), um den Widerstand des Sensorelements (8) zu messen und dadurch die NO<sub>x</sub>-Konzentration des zu messenden Gases zu detektieren,

einen Katalysator (6), der in Bezug auf das Sensorelement in Strömungsrichtung des zu messenden Gases stromauf angeordnet ist, wobei der Katalysator dazu ausgebildet ist, wenn er mit dem zu messenden Gas in Kontakt kommt, das Partialdruckverhältnis von NO und NO<sub>2</sub> im Gas ins Gleichgewicht zu bringen und CO aus dem Gas zu entfernen,

eine Heizeinrichtung (7), die in Bezug auf das Sensorelement (8) und den Katalysator (6) angeordnet ist, um die Temperatur des Sensorelements und des Katalysators konstant zu halten, sowie

einen O<sub>2</sub>-Sensor (9), um die O<sub>2</sub>-Konzentration des zu messenden Gases zu detektieren,

worin das Messmittel (2) dazu angeordnet ist, eine Einstellung des Messwerts vom Sensorelement (8) auf Basis der O<sub>2</sub>-Konzentration durchzuführen, die vom O<sub>2</sub>-Sensor detektiert wird, um die NO<sub>2</sub>-Konzentration des Gases zu bestimmen.

2. NO<sub>x</sub>-Sensor nach Anspruch 1, worin das Oxid des Sensorelements (8) ein Metalloxid-Halbleiter ist.
3. NO<sub>x</sub>-Sensor nach Anspruch 2, worin der Metalloxid-Halbleiter SnO<sub>2</sub>, TiO<sub>2</sub> oder In<sub>2</sub>O<sub>3</sub> ist.
4. NO<sub>x</sub>-Sensor nach Anspruch 1, 2 oder 3, worin der Katalysator (6) ein Edelmetall oder ein Oxid ist.
5. NO<sub>x</sub>-Sensor nach Anspruch 4, worin der Katalysator (6) ein Edelmetall ist, das aus Platin, Rhodium und Gold ausgewählt ist.
6. NO<sub>x</sub>-Sensor nach Anspruch 5, worin der Katalysator (6) ein Manganoxid, ein Kobaltoxid oder ein Zinnoxid ist.
7. Verfahren zum Messen der NO<sub>x</sub>-Konzentration unter Verwendung eines Sensors nach einem der vorangegangenen Ansprüche.

## Revendications

1. Un capteur pour NOx présentant

un élément capteur (8) fabriqué en un oxyde dont la résistance varie en dépendance de la concentration en NOx d'un gaz à mesurer,  
des moyens de mesure (2) pour mesurer la résistance de l'élément capteur (8) et détecter ainsi la concentration en NOx du gaz à mesurer,  
un catalyseur (6) disposé à l'amont par rapport audit élément capteur dans une direction d'écoulement du gaz à mesurer, ledit catalyseur étant adapté, lorsqu'il est mis en contact par le gaz à mesurer, à amener à l'équilibre le rapport des pressions partielles de NO et de NO<sub>2</sub> dans le gaz et à retirer le CO du gaz,  
un organe de chauffage (7) disposé par rapport à l'élément capteur (8) et au catalyseur (6) pour maintenir une température constante de l'élément capteur et du catalyseur, et  
un capteur pour O<sub>2</sub> (9) permettant de détecter la concentration en O<sub>2</sub> du gaz à mesurer,  
dans lequel lesdits moyens de mesure (2) sont disposés pour effectuer un réglage de la valeur de mesure issu de l'élément capteur (8) sur la base de la concentration en O<sub>2</sub> détectée par ledit capteur pour O<sub>2</sub>, afin de déterminer la concentration du gaz en NO<sub>2</sub>.

2. Un capteur pour NOx selon la revendication 1, dans lequel ledit oxyde de l'élément capteur (8) est un semi-conducteur à oxyde métallique.
3. Un capteur pour NOx selon la revendication 2, dans lequel ledit semi-conducteur à oxyde métallique est SnO<sub>2</sub>, TiO<sub>2</sub> ou In<sub>2</sub>O<sub>3</sub>.
4. Un capteur pour NOx selon la revendication 1, 2 ou 3, dans lequel ledit catalyseur (6) est un métal précieux ou un oxyde.
5. Un capteur pour NOx selon la revendication 4, dans lequel ledit catalyseur (6) est un métal précieux choisi parmi le platine, le rhodium et l'or.

## EP 0 737 859 B1

6. Un capteur pour NOx selon la revendication 5, dans lequel ledit catalyseur (6) est un oxyde de manganèse, un oxyde de cobalt ou un oxyde d'étain.
7. Un procédé de mesure de la concentration de NOx en utilisant un capteur selon une quelconque des revendications précédentes.

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**FIG. 1**

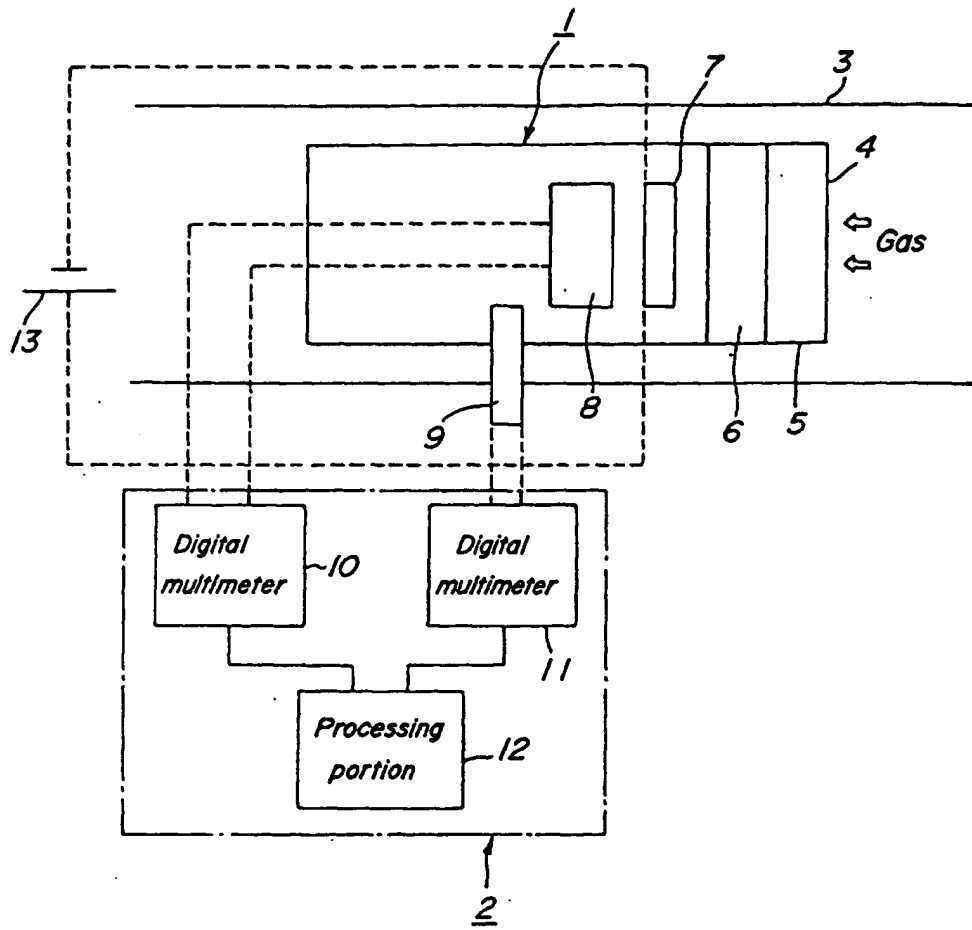


FIG. 2

